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Graphical Abstract

Ag NPs decked GO composite as a competent and reusable catalyst for 'ON WATER' chemoselective synthesis of pyrano[2,3-c:6,5-c']dipyrazol]-2-ones

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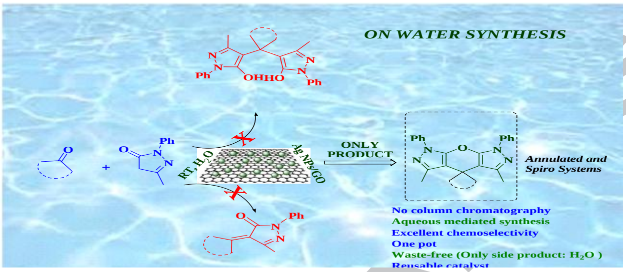

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Ag NPs decked GO composite as a competent and reusable catalyst for 'ON WATER' chemoselective synthesis of pyrano[2,3-c:6,5-c']dipyrazol]-2-ones

Anshu Dandia*[a], Shyam L. Gupta[a], Aayushi indora [a], Pratibha Saini[a], Vijay Parewa*[a], Kuldeep S. Rathore[b]

[a] *Centre of Advanced Studies, Department of Chemistry,*
University of Rajasthan, Jaipur-302004, India
[b]*Semiconductor and Polymer Science Laboratory. Department of Physics, University of Rajasthan, Jaipur*

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ABSTRACT

We have synthesized and characterized Ag NPs decked GO composite and studied its role as reusable catalyst for the 'ON WATER' chemoselective synthesis of pyranodipyrazolones via the reaction of different carbonyl compounds with 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one. This method illustrates significant selectivity for pyranodipyrazolones over arylmethylene bispyrazolols and arylmethylenepyrazolones. Synergistic effect of heterogenic nature of water with reactants and Ag NPs/GO had profuse outcome on reaction as indicated by high TOF (18.03x 10^{-5} mol g^{-1} min^{-1}). Furthermore, catalyst was recycled for 7-times without significant loss of activity

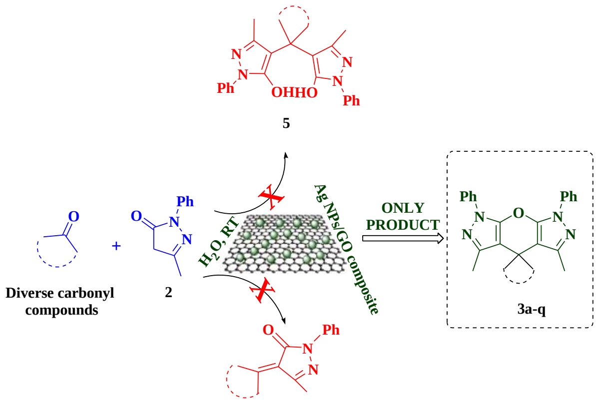
Pyranopyrazoles play essential role as biologically active compounds and represent an interesting template for medicinal chemistry. Many of these compounds are known for their antimicrobial[1], insecticidal[2], anti-inflammatory[3] and anticancer activities[4]. Furthermore, pyranopyrazoles show molluscicidal activity[5] and are identified as screening kit for Chk1 kinase inhibitor[6]. They also find applications as pharmaceutical ingredients and biodegradable agrochemicals[7]**.** Some pyrano[2,3-*c*]pyrazoles have been evaluated for their bovine brain adenosine $A_{1,}$ A_{2A} receptor binding affinity. Also, these pyranopyrazoles are of interest because of their structural similarity to a wide variety of flavones and flavanones that exhibit interesting biological activity[8]. Despite their pharmaceutical, industrial, and synthetic importance, only a few methods for their preparation have been reported so far[9].

A cautious study dictates that most of the methodologies suffer some drawbacks e.g: reaction under high temperatures, use of expensive and environmentally harmful catalysts, harsh reaction conditions, formation of a mixture of products, multi step procedure, longer reaction times and involvement of volatile organic solvents in high quantity which limits the broad use of these methodologies. Moreover, the major drawback of almost all existing methods is the sinking turn over number (TON) or turn over frequency (TOF),as the catalysts are destroyed in the work-up process and cannot be recovered or reused, which is vital from the industrial point of view. As a result, the development of new synthetic methods for this purpose remains an attractive goal.

An exponentially growing research field of nanocatalysis in modern science[10] has met the challenges of energy and sustainability. In this context, Ag NPs are being widely used in numerous areas due to their various distinctive properties[11,12,13]. But, the practical applications of Ag NPs in catalytic science are often hindered by their self-aggregation[14-15]. Hence, development of dispersed & stable Ag NPs substrates has been become a topic of immense concern. Moreover, among diverse carbon nanomaterials, graphene oxide can be considered as a heterogeneous support for various other nanoparticles,[16] as they exhibit highly accessible oxygen-containing functionalities or binding sites with intrinsically high surface area.

Besides this, water has attracted considerable interest in the context of sustainable chemistry, as it can be used as an efficient reaction medium for many nanocatalytic routes.[17] The unique structure and physicochemical properties of water lead to particular interactions which might greatly facilitates the reaction course[18]. Thus, attainment of sustainable synthetic strategy inherently involves implementation of developed catalytic processes in water to achieve greener syntheses.

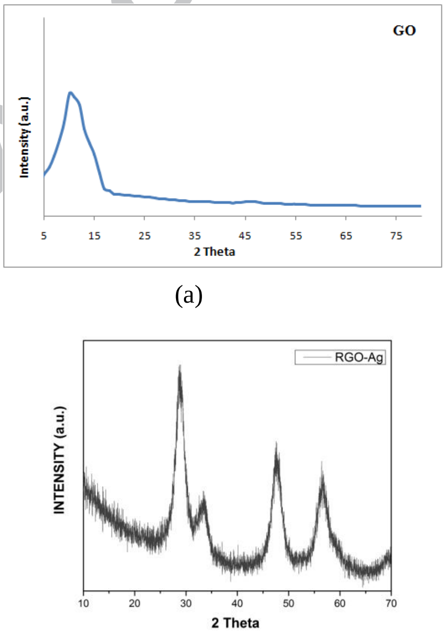
In the above regards and as a consequence of our interest in development of new nanocatalytic processes and sustainable synthesis of biologically important scaffolds[19], we herein report, 'on-water' chemoselective synthesis of pyranodipyrazolones *via* the reaction of various carbonyl compounds with 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one using Ag NPs decorated reduced graphene oxide (Ag NPs/GO) composite which is a facile, leach free and easily recyclable heterogeneous catalyst at room temperature (**Scheme 1**).



Scheme 1: Chemoselective synthesis of pyranodipyrazolones

The product distribution of the reaction of various carbonyl compounds with 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one has been reported to strongly depend on the reaction conditions. The reaction gave a mixture of compounds[20], arylmethylenepyrazolones (**4**), arylmethylene bispyrazolols (**5**) and pyranodipyrazolones (**3**). Sometimes **4** and **5** have been isolated as the main product instead of pyranodipyrazolones[21]. This phenomenon triggered our enthusiasm towards the exclusive formation of the pyranodipyrazolone derivatives.

GO, Ag NPs/GO and Ag NPs/rGO nanocomposites were fabricated by simple one-pot chemical route[19f] and well characterized by XRD, TEM, SEM and EDX analyses. XRD patterns of GO, Ag NPs/rGO and Ag NPs/GO composite are given in Fig.1 (a), (b) and Fig.2 respectively. For GO sheets, a sharp characteristic peak is observed due to the (001) reflection of GO. In the XRD pattern of Ag NPs/rGO and Ag NPs/GO composite, the diffraction peaks for crystallographic planes of Ag NPs phase with rGO and Ag NPs phase with GO are observed. The average particle size of Ag NPs was ~20 nm on the basis of Scherrer formula. In TEM analysis (Fig.3), GO sheet showed modification of plenty of Ag NPs (~ 28 nm) after blending the GO with silver colloids. Ag NPs were adsorbed on both sides of GO. In SEM analyses, Ag NPs were completely distributed on GO indicating strong interactions between GO and Ag NPs (Fig. S1a; see ESI). According to EDX analysis, the Ag NPs/GO composite contains C, O, and Ag. The signals of C and O originated due to GO and that of Ag resulted from the decorated Ag NPs. The % amount of various elements is shown in respective figure (Fig. S2; see ESI).



(a)

(b)

Fig. 1. XRD patterns of graphene oxide (a) and Ag NPs/rGO (b)

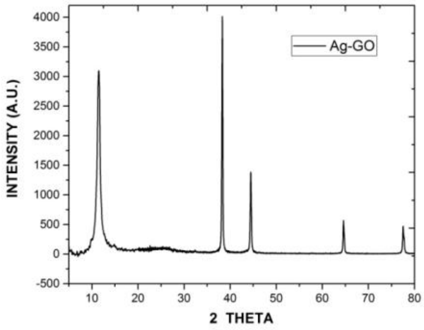


Fig. 2. XRD patterns of Ag NPs/GO composite

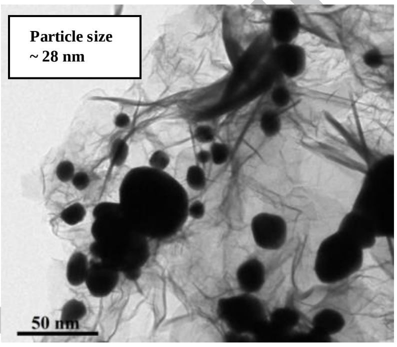


Fig. 3. TEM image of Ag NPs/GO composite

To appraise the catalytic activity of prepared nanocomposite for the "on water" synthesis of pyrano[2,3-c:6,5-c']dipyrazol]-2-ones, reaction of 4-bromo benzaldehyde **1** and 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one **2** served as model reaction at room temperature. A controlled experiment was investigated in the absence of catalyst. But the result indicates the need of a catalyst. Thus in order to achieve suitable conditions, we chose various catalysts and the results are summarized in Table 1. As compared to the blank reaction, analogous results were found in CAN (ceric ammonium nitrate), PTSA (*p*-toluenesulfonic acid), Sulfamic acid and L-Proline. Moreover, silver based bulk catalyst could only afford the desired compound in low yields. When the reaction was carried out in the presence of catalytic amount of Ag NPs, the desired product 3f was isolated in moderate yield. Further GO and rGO sheets also gave good yields (Table 1, entry 9-10). However, the best result in terms of turnover frequency (TOF: number of moles of product produced per gram of catalyst used per min[22, 19f]) attained by Ag NPs/GO composite catalyst (10 wt% loading, TOF = 18.03 x 10^{-5} mol g^{-1} min^{-1}). It was found that 10 wt% of Ag NPs/GO composite is sufficient to push the reaction forward. Any excess amount did not show further increase in yield. Additionally, we have also checked the catalytic activity of AgNPs/rGO composite on this reaction, lower catalytic activity was observed as compared to AgNPs/GO. This may be explained due to presence of reduced or lower catalytic sites in AgNPs/rGO composite as compared to AgNPs/GO.

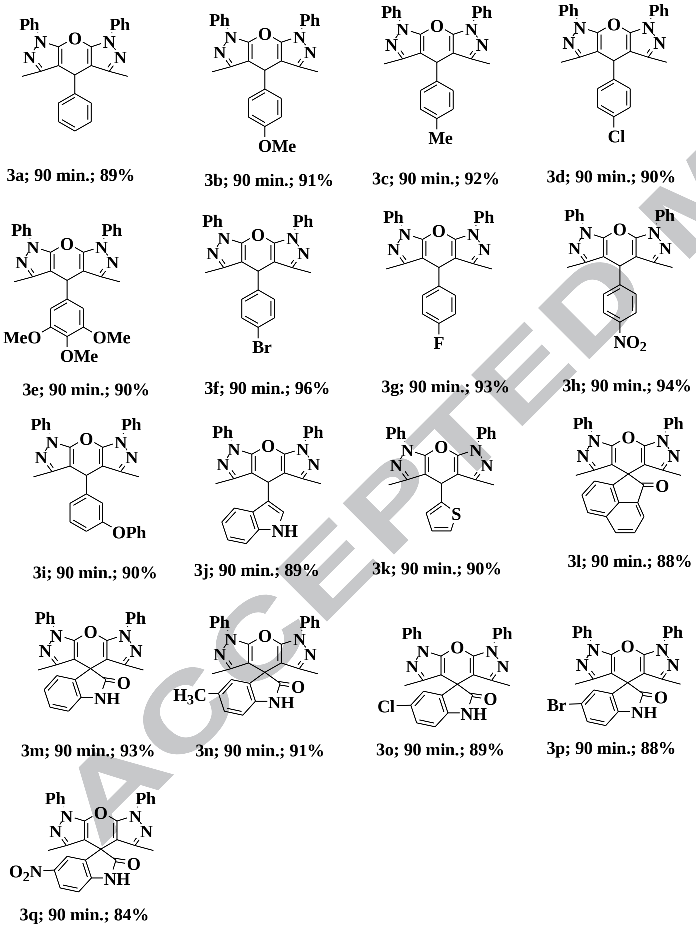
Table 1. Comparison of catalytic activity of Ag NPs/GO composite with other catalytic systems in different conditions for synthesis of 4-(4-bromophenyl)-3,5-dimethyl-1,7-diphenyl-4,7-dihydro-1*H*-pyrano[2,3-c:6,5-c']dipyrazole (**3f**)[a].

S. No.	Catalyst	Solvent	Time(h)	Yield (%)[b]	TON ($x10^{-5}$ mol g^{-1})	TOF ($x10^{-5}$ mol g^{-1} min^{-1})[c]
1.	-	H_2O	4	60	-	-
2.	CAN	H_2O	4	63	1065	4.44
3.	PTSA	H_2O	4	65	1099	4.58
4.	Sulfamic acid	H_2O	4	62	1048	4.36
5.	L-Proline	H_2O	4	62	1048	4.36
6.	AgCl	H_2O	2	68	1150	9.58
7	$AgNO_3$	H_2O	2	67	1133	9.44
8.	Ag NPs	H_2O	2	76	1286	10.71
9.	GO	H_2O	2	72	1218	10.15
10.	rGO	H_2O	2	68	1150	9.58
11.	Ag NPs/GO	H_2O	1.5	96	1622	18.03
12.	Ag NPs/GO[d]	H_2O	1.5	96	1021	11.35
13.	Ag NPs/GO[e]	H_2O	1.5	40	1432	15.91
14.	Ag NPs/GO	H_2O/ MeOH(1:1)	1.5	72	1218	13.53
15.	Ag NPs/GO	MeOH	1.5	58	980	10.88
16.	Ag NPs/GO	CH_3CN	1.5	52	877	9.75
17.	Ag NPs/GO	THF	1.5	Trace	-	-
18.	Ag NPs/GO	DCM	1.5	Trace	-	-
19.	Ag NPs/GO	EtOH	1.5	54	912	10.12
20	Ag NPs/GO	Toluene	1.5	Trace	-	-
21	Ag NPs/GO	Neat	1.5	32	541	6.00
22	Ag NPs/rGO	H_2O	1.5	78	1320	14.66

[a] Reactions were performed using 1:2 ratio of 4-bromo benzaldehyde **1** and 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one **2** at room temperature with 10 wt% of the catalyst. [b] Isolated yield. [c] TOF is defined as the number of moles of product produced per gram of catalyst used per min. [d] with 15 wt% of the catalyst [e] with 5 wt% of the catalyst

The effect of various solvents on the model reaction was also conducted. When organic solvents such as DCM, THF and toluene were used, trace amount of desired product was detected. While polar protic solvents accelerate the reaction. Additionally, we carried out the reaction in heterogeneous as well as homogeneous aqueous systems. Methanol was used to make the reaction homogeneous in water. Under analogous conditions, higher conversion of reactants into the product was observed in the heterogeneous compared to the homogeneous conditions. This result indicates that using only water as the solvent in the reaction afforded excellent product yield. Hence, apart from the catalytic role of Ag NPs/GO composite which activates the carbonyl groups of the reactants, heterogeneity also plays crucial role in rate accelerations. Furthermore, it can also be expected that, due to the good dispersion of this nanocomposite in water as compared to other solvents, most of the catalytic sites of Ag NPs/GO composite were exposed to the reaction environment. The subsequent solvent-free synthesis takes virtually many hours and gave poor result, which shows that the rate improvement is not the individual effect of an increase in the concentration of reactants (Table 1, entry-21). The on-water idea assists easy isolation of solid product from the reaction mixture.

The general efficiency of this protocol was then studied for the synthesis of a variety of pyranodipyrazolone derivatives and the results are summarized in Fig.4. A series of aromatic aldehydes bearing either electron-donating or electron-withdrawing groups on aromatic ring were investigated. The substituting group on the phenyl ring did not seem to affect the yield of product or the rate of the reaction significantly. To demonstrate the versatility of this technique for generating variety of pyranodipyrazolone derivatives, various isatin**s**, heterocyclic aldehydes and acenapthaquinone were also tested. These carbonyl compounds react smoothly with 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one **2** to afford the desired products in excellent yields. Further, ICP-AES analysis showed that there was no metallic leaching in the final product.



3a; 90 min.; 89%

3b; 90 min.; 91%

3c; 90 min.; 92%

3d; 90 min.; 90%

3e; 90 min.; 90%

3f; 90 min.; 96%

3g; 90 min.; 93%

3h; 90 min.; 94%

3i; 90 min.; 90%

3j; 90 min.; 89%

3k; 90 min.; 90%

3l; 90 min.; 88%

3m; 90 min.; 93%

3n; 90 min.; 91%

3o; 90 min.; 89%

3p; 90 min.; 88%

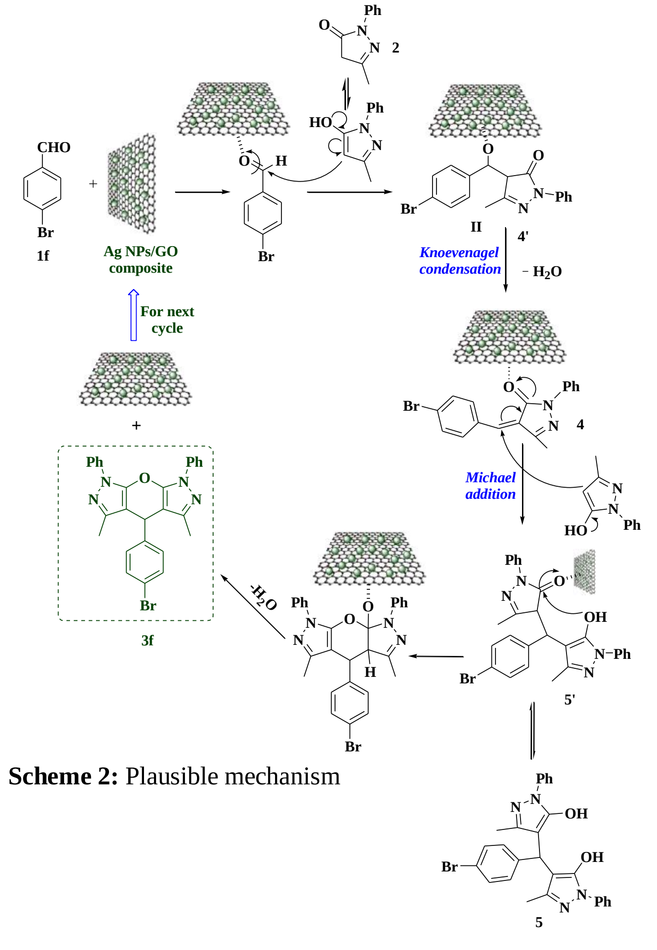
3q; 90 min.; 84%

Fig. 4. Products of chemoselective synthesis of pyrano[2,3-c:6,5-c']dipyrazol]-2-ones

In the reaction of carbonyl compounds with 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one, the formation of the required pyranodipyrazolones was accompanied by the occurrence of arylmethylene bispyrazolols and arylmethylenepyrazolones as side products and sometimes these products have been isolated as the main products. The present protocol resulted in pyranodipyrazolones selectively and exclusively. The structure of the products was established by IR, ^{1}H, ^{13}C NMR and mass spectrometric studies. For instance, IR spectrum of the product **3f** showed important absorption band at 1598 cm^{-1} due to the presence of C=N group in the cyclic ring system while the band at 1152 cm^{-1} was due to the presence of cyclic ether (pyran) functionality. In ^{1}H NMR singlet at δ 2.31 was assigned to the methyl protons of pyrazolone unit while singlet at δ 4.94 was attributed to the methane (CH) proton and the region between δ 7.18-7.71 was due to the 14 aromatic protons. In ^{13}C NMR study, peak at δ 150.9 confirmed the presence of cyclic ether carbon associated with pyrazolone unit while peak at δ 32.5 can be attributed to the methane CH carbon. The structure of product **3f** was further established by mass spectrometry which showed a molecular ion peak [M+ H$_2$O]$^+$ at m/z 516.

In IR spectrum, the lack of the peak of carbonyl group and –OH ruled out the formation of 1-phenyl-3- methyl-4-arylmethylenepyrazol-5-ones (**4**) and 4,4'-(arylmethylene)-bis-(3-methyl-1-phenyl-1*H*-pyrazol-5-ols (**5**) respectively instead of pyrano[2,3-c:6,5-c']dipyrazol]-2-one derivatives. This was also confirmed by the absence of characteristic peak of vinylic proton and –OH in ^{1}H NMR spectrum for **4** and **5** correspondingly.

A plausible mechanism for the formation of the product is presented in **Scheme 2**. It involves electrophilic activation by coordinating with the Lewis acid sites of Ag NPs/GO composite. Initially, increase in the reactivity of carbonyl group of 4-bromo benzaldehyde **1f** occurs which then reacts with one unit of pyrazolone **2** through Knoevenagel condensation to form Knovengeal adduct **4.** Further Ag NPs/GO composite activates the adduct **4** by coordinating with oxygen and facilitates the Michael addition of second pyrazolone unit and forms hydroxyl derivate **5'**, which upon subsequent cyclization gives the desired product **3f** by loss of water molecule and finally, releasing the catalyst for the next cycle. Hence, it is assumed that the higher and well dispersed Lewis acid sites of Ag NPs/GO composite enhances the reactivity of reactant and intermediate towards the Knovengeal -Michael addition sequence followed by ensuing cyclization. Due to this rationale, the present protocol results in pyranodipyrazolones selectively and exclusively instead of **4** and **5**.



Scheme 2: Plausible mechanism

Recycling experiments were also being performed for the model reaction. Upon completion of the reaction, the resulting solid precipitate was filtered and dried along with the Ag NPs/GO composite. Then, the solid precipitate was dissolved in ethanol and the catalyst was recovered by filtration. The catalyst was washed with acetone and reused in subsequent 7 reaction cycles without any significant loss in its catalytic activity (Fig. 5). Up to 99% ,catalyst recovery has been observed during the process. TEM and SEM image of reused nanocomposite was also recorded which shows that the structural integrity remains unaltered after the reaction and thus proves the efficiency of nanocomposite as a recyclable catalyst (Fig. S1b, S3b; see ESI)..

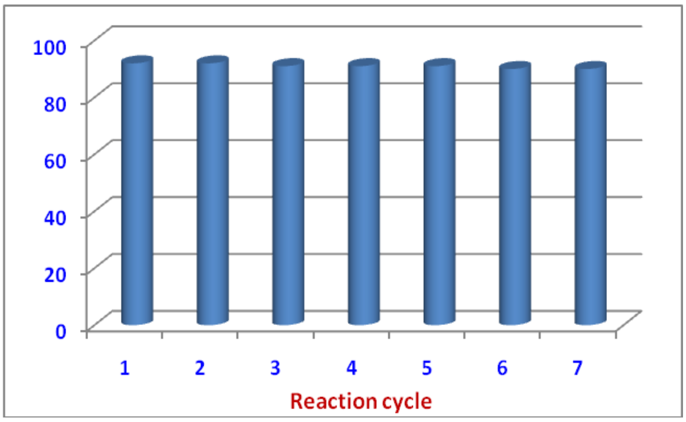


Fig. 5 Recyclability of Ag NPs/GO composite

Hence, we conclude that a highly efficient protocol has been developed for the "on water" chemoselective synthesis of structurally complex and diverse pyrano[2,3-c:6,5-c']dipyrazol]-2-one derivatives catalyzed effectively by Ag NPs/rGO composite. Moreover, this method can be considered as an ideal tool for green synthesis because it minimizes the generation of waste along with the formation of multiple bonds in a single step. The process has high atom economy and is ecologically benign, since only two molecules of water are lost. Three rings of the fused-ring framework were constructed during the reaction and in addition, catalyst could be easily recovered and recycled at least 7 times without significant loss of catalytic activity.

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Supplementary Material

Supporting data (detailed experimental procedures and spectral data of compounds) associated with this article can be found in ele

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Highlights

- On water chemo-selective organic synthesis.
- Synergistic effect of Ag NPs/GO composite and water.
- pyrano[2,3-c:6,5-c']dipyrazol]-2-one formed selectively
- Easy recovery and high recyclability of catalyst.